BIO ORGANIC CHEMISTRY

An International Journal

EDITOR

E. E. van Tamelen

EDITORIAL ASSOCIATES

D. H. R. Barton *A. Kornberg* *Lord Todd*

HONORARY BOARD OF ADVISORS

D. Arigoni
A. R. Battersby
K. Bloch
R. Breslow
M. Calvin
R. W. Holley
W. S. Johnson
T. Kametani
D. E. Koshland, Jr.
H. M. McConnell
A. I. Scott
L. L. M. van Deenen

Volume 3, 1974

ACADEMIC PRESS
New York and London
A Subsidiary of
Harcourt Brace Jovanovich, Publishers

Copyright © 1974 by Academic Press, Inc.

ALL RIGHTS RESERVED

No part of this publication may be reproduced or transmitted in any form, or by any means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without permission in writing from the copyright owner.

CONTENTS OF VOLUME 3

NUMBER 1, MARCH 1974

JOHN H. YOUNG, EPHRAIM F. KORMAN, AND JEROME MCLICK. On the Mechanism of ATP Synthesis in Oxidative Phosphorylation: A Review..... 1

C. G. OVERBERGER AND C. J. PODSIADLY. Conformational Effects and Cooperative Interactions in Poly[5(6)-vinylbenzimidazole]-Catalyzed Solvolyses of Anionic, Long-Chain Substrates..... 16

C. G. OVERBERGER AND C. J. PODSIADLY. Cooperative Effects Involved in Esterolytic Reactions of Cationic Long Chain Esters Catalyzed by Benzimidazole-Containing Polymers..... 35

JEAN-JACQUES BÉCHET, ROBERT ALAZARD, ALAIN DUPAIX, AND COLETTE ROUCOUS. Intramolecular Participation of the Amide Group in the Hydrolysis of *p*-Nitrophenyl *N*-(bromoacetyl) Anthranilate..... 55

N. C. DENO, DOUGLAS G. POHL, AND HARRY J. SPINELLI. Sterically Hindered Chlorinating Agents that Relate to Terminal Biological Oxidations..... 66

KAZUO T. SUZUKI AND SHIGEO NOZOE. Biosynthesis of an Antibiotic, Siccanin.. 72

GEORGE M. STEINBERG AND MORTON L. MEDNICK. Phosphonofluoridate Inhibition of Acetylcholinesterase: an Exceptionally Rapid Reactant..... 81

NUMBER 2, JUNE 1974

EDMOND J. GABBAY AND KARL SANFORD. Dissymmetric Recognition of the Helical Sense of Deoxyribonucleic Acid and Evidence for Binding of Reporter Molecules from the Minor Groove of DNA..... 91

B. JASTORFF AND W. FREIST. Synthesis and Biological Activities of Cyclic AMP Analogs Modified in the 1,2 and 2′-Positions..... 103

CLAUDIO TONIOLO AND GIAN MARIA BONORA. Phenylalanine Oligopeptides: Synthesis, Polarimetric and Ultraviolet Absorption Studies..... 114

EVARISTO PEGGION, MANLIO PALUMBO, GIAN MARIA BONORA, AND CLAUDIO TONIOLO. Phenylalanine Oligopeptides: Circular Dichroism Studies in Solution 125

MIKLOS BODANSZKY, AGNES BODANSZKY, YAKIR S. KLAUSNER, AND SAMI I. SAID. A Preferred Conformation in the Vasoactive Intestinal Peptide (VIP). Molecular Architecture of Gastrointestinal Hormones 133

NORMAN J. OPPENHEIMER AND NATHAN O. KAPLAN. Determination of the Absolute Stereospecificity of the Enzymatic Reduction of NAD^+ Analogs by Means of the Primary Acid Cyclization Reaction 141

FRANK A. SEDOR, DAN G. JACOBSON, AND EUGENE G. SANDER. The Dehalogenation of Iodouracil by Cysteine. Intramolecular General-Acid Catalysis of Cysteine Addition to 5-Iodouracil 154

B. A. HUMPHRIES, M. S. ROHRBACH, M. S. BROOKHART, AND J. H. HARRISON. Kinetics of Formation of the 4,4′-Bis-Dimethylaminodiphenyl Carbonium Ion (BDC^+) and its Reaction with Sulfhydryl Residues 163

H. BROCKERHOFF. Regulation of Enzyme Activity by Enzyme Orientation: A Hypothesis 176

MURRAY GOODMAN, ALVIN STEINFELD, ALAN TONELLI, UGO LEPORE, MANLIO PALUMBO, AND BERNARD DONZEL. Synthesis and Conformational Analysis of Cyclo-TRI[L-Valyl-D-Hexahydromandelyl] 184

F. C. PENNINGTON, N. B. BOETTCHER, AND J. J. KATZ. Ring V Reactions of Chlorophylls and Pheophytins with Amines 204

MICHAEL J. BOLAND, MICHAEL J. HARDMAN, AND IAN D. WATSON. Rate Enhancement by Catalytic Groups in Enzymes. Imidazole Catalysis of the Hydrolysis of *N,O*-Di-acetylserinamide as a Model for General Base Catalysis in Chymotrypsin 213

FRANK A. SEDOR, DAN G. JACOBSON, AND EUGENE G. SANDER. The Addition of Bisulfite to 5-Fluorouracil. Evidence for a Change in Rate Determining Step 221

A. IAN SCOTT, EUN LEE, AND CRAIG A. TOWNSEND. On Corrin Biogenesis 22

A. IAN SCOTT, L. C. BEADLING, N. H. GEORGOPAPADAKOU, AND C. R. SUBBARAYAN. Biosynthesis of Polyketides. Purification and Inhibition Studies of 6-Methylsalicylic Acid Synthase 238

NUMBER 3, SEPTEMBER 1974

A. Robert Goldfarb. Reactions of the Amino Groups in Ribonuclease A. I. Kinetic Studies 249

A. Robert Goldfarb, Douglas N. Buchanan, and Donald E. Sutton. Reactions of the Amino Groups in Ribonuclease A. II. Identification of Reactive Amino Groups in Ribonuclease 260

Mendel Friedman and L. David Williams. Stoichiometry of Formation of Ruhemann's Purple in the Ninhydrin Reaction 267

A. Ian Scott and Leslie Beadling. Biosynthesis of Patulin. Dehydrogenase and Dioxygenase Enzymes of Penicillium Patulum 281

Walter G. Niehaus, Jr. Thiol-Catalyzed cis-trans Isomerization of Oleic Acid 302

Yukio Kakuda and Delbert D. Mueller. Hydrogen-Deuterium Exchange of a Primary Amide as a Model for Asparagine and Glutamine Exchange in Proteins 311

Miklos Bodanszky, Cynthia Yang Lin, and Sami I. Said. The Vasoactive Intestinal Peptide (VIP). VI. The 17-Norleucine Analog of the Sequence 14-28 320

William B. Gruhn and Myron L. Bender. Enzyme Models. The Attachment of *N*-Methylhydroxamic Acid to Cyclohexaamylose. Its Reactivity and Specificity with Phenyl Esters 324

C. E. Castro, Colin Robertson, and Harry Davis. The Reactions of Octaethylporphyrin and Its Iron (II) and Iron (III) Complexes with Free Radicals 343

Michael D. Corbett. Hydroxamic Acids from the Reaction of Active Acetaldehyde with Aromatic Nitroso Compounds 361

NUMBER 4, DECEMBER 1974

Fritz Hansske, Mathias Sprinzl, and Friedrich Cramer. Reaction of the Ribose Moiety of Adenosine and AMP with Periodate and Carboxylic Acid Hydrazides 367

Gerald Gold and Ronald Bentley. The Conversion of *S*-Adenosyl-L-Methionine to Stipitatic Acid by Extracts of *Penicillium stipitatum* 377

IAIN M. CAMPBELL. Review: Incorporation and Dilution Values—Their Calculation in Mass Spectrally Assayed Stable Isotope Labeling Experiments.... 386

A. IAN SCOTT. Review: Biogenetic-type Synthesis of the Indole Alkaloids..... 398

T. KAMETANI, K. FUKUMOTO, AND F. SATOH. Review: The Syntheses of Isoquinoline Alkaloids and Related Compounds by Biogenetic Type Reactions 430

AUTHOR INDEX..... 499

SUBJECT INDEX..... 500

Information for Authors

Bioorganic Chemistry: An International Journal publishes accounts of research on the organic and physical organic chemistry of biological or biologically related reactions. Within this context, manuscripts treating the following topics are suitable for submission:

> New enzymic reactions in which the chemistry is apparent by way of starting material and product structures; the elucidation of enzyme reaction mechanisms from the physical organic standpoint; the isolation and structure determination of new natural products which have implications for basic biological reactions; biogenetic-type organic synthesis, in which there are executed non-enzymic reactions based upon substrate behavior in biological processes; the synthesis and behavior of model enzymes; the molecular structure and chemical behavior of enzymes; prebiotic and evolutionary organic chemistry; the chemistry of biopolymers; molecular pharmacology.

Regular articles must feature novel, unpublished material or represent full accounts of findings published earlier in preliminary form. Contributions may be either experimentally oriented or entirely theoretical. Articles that are sensibly speculative or constitute new interpretations of older findings are appropriate. Although there is no provision for expedited publication of preliminary disclosures, the editors will consider manuscripts which feature significant new results, described briefly and without a separate experimental section.

Reviews containing apposite subject material are welcome. An acceptable review may embrace the results of various workers in a given area or may feature recent developments from the author's own laboratory. A review that is distinguished by a novel interpretation or presentation of earlier findings is especially suitable. Announcements of meetings, new books, or other developments of interest to the bioorganic chemist will be printed upon request. Manuscripts are considered for publication on the proviso that they have not been, nor will be, published elsewhere.

Address all submitted manuscripts and correspondence to:

Dr. Eugene E. van Tamelen
Editor, *Bioorganic Chemistry*
Department of Chemistry
Stanford University
Stanford, California 94305.

Manuscripts should be written in a clear and accurate fashion with careful attention to detail. Submit manuscripts (preferably in English) in triplicate, including the original typewritten copy, with copies of graphs, drawings, organic structural formulas, etc., suitable for direct reproduction by the photoengraver. All material (including tables, legends, reference lists, and footnotes) should be typed double spaced on one side of $8\frac{1}{2} \times 11$-in. white bond paper with 1-in. margins on all sides. Each page of the manuscript should be numbered. Page 1 should contain the article title, author's name (without degrees), affiliation, a short running title (not exceeding 45 letters and spaces), and an address to which proof should be mailed. Page 2 should contain a short abstract. Acknowledgments may be included as a separate section.

All nomenclature should be simple, unambiguous, and in conformity with the conventions developed by Chemical Abstracts and the International Union of Pure and Applied Chemistry.

Abbreviations should be in accordance with the International System (SI) as adopted by the 11th General Conference on Weights and Measures. Common abbreviations are: meter, m; centimeter, cm; millimeter, mm; micrometer, μm; nanometer, nm; kilogram, kg; gram, g; milligram, mg; microgram, μg; nanogram, ng; milliliter, ml; microliter, μl; molar, M; millimolar, mM; micromolar, μM; normal, N; millicurie, mCi; microcurie, μCi; counts per minute or second, count/min or count/sec; disintegrations per minute or second, dpm or dps; centigrade, °C; seconds, sec; minutes,

min; hours, hr; standard deviations, SD; standard error, SE; percent, %; melting point, mp; boiling point, bp; calorie, cal; kilocalorie, kcal; nuclear magnetic resonance, nmr; infrared, ir; ultraviolet, uv; number, No.; Ångstrom units, Å; cycles per second, cps; parts per million, ppm; equation, Eq.

Tables must appear on a separate sheet with a descriptive title typed double spaced above the table. Tables must be numbered consecutively with Arabic numerals in order in the text.

Figures and graphs are to be numbered consecutively in Arabic numerals and cited in order in the text; legends should be typed double spaced on a separate sheet. Graphs should be plotted with black India ink on white paper no larger than 8.5 × 11 in., with coordinates properly labeled; grid lines that are to show in the engraving should be inked in black. Original drawings no larger than $8\frac{1}{2} \times 11$ in. (21 × 27.5 cm) are preferred. The following standard symbols should be used in the legends to the figures because they are readily available to the printers:

▲ □ ■ ○ ● ⊙ × ◈ ◆.

Photographs should be kept to a minimum and should be glossy prints with strong contrasts; the magnification should be indicated by a scale where possible.

Structural formulas and chemical equations should be typed or drawn with care, and arranged to fill space economically. Since chemical structures will be engraved directly from manuscript copy, authors are asked to prepare such material using appropriate templates and to check it carefully before manuscript submission.

Footnotes should be designated in text by superscript numbers and listed on a separate sheet, starting with the title; in tables they should be noted by superscript letters and placed at the bottom of the page containing the table.

References to the literature should be cited in the text by underlined Arabic numerals in parentheses. They must appear on a separate sheet, listed in numerical order—i.e., in accordance with order of citation in the text. Styling of references should conform to the following format (authors should refer to Chemical Abstracts' *Service Source Index* for styling of journal titles):

1. L. G. Longsworth, R. K. Cannan, and D. A. Macinnes, *J. Amer. Chem. Soc.* **62**, 2580 (1940).
2. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," 2nd ed., Vol. 1, pp. 15–20. Academic Press, New York, 1970.
3. L. G. Longsworth, "Electrophoresis" (M. Bier, Ed.). Academic Press, New York, 1969.

Galley proofs will be sent to the senior author. Authors will be charged for alterations in excess of 10% of the cost of composition.

Fifty reprints of each article will be supplied free of charge. Additional reprints may be purchased; an order form will accompany proofs. There are no publication charges.